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(54) Title: MULTIFUNCTIONAL ACID MODIFIERS FOR ACID-CONTAINING POLYMER SYSTEMS

(57) Abstract

A polymer composition comprising: (a) 100 parts by weight of an ionomeric resin; and (b) from about 1 to about 20 parts by weight f a polycarboxylic acid or a salt thereof.

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MULTIFUNCTIONAL ACID MODIFIERS FOR ACID-CONTAINING POLYMER SYSTEMS

Field of the Invention:

The present invention generally relates to polycarboxylic acids used as modifiers for acid-containing polymers. More particularly, by introducing polycarboxylic acids into acid-containing polymers and ionomeric resins, the rheological properties of the resins can be modified.

Background of the Invention:

Ionomeric resins are polymers containing interchain ionic bonding. Ionomeric resins are ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. In some instances, an additional softening comonomer such as an acrylic ester can also be included to form a terpolymer. The pendent ionic groups in the ionomeric r sins interact to form ion-rich aggregates contained in a non-polar matrix.

The ionic copolymers generally comprise one or more α-olefins and

from about 9 to about 30 weight percent of α,β-ethylenically unsaturated mono- or dicarboxylic acid, the basic copolymer neutralized with metal ions to the extent desired. Suitable olefins for use in preparing the ionomeric resins include ethylene, propylene, butene-1, hexane-1, and the like. Unsaturated carboxylic acids include acrylic, methacrylic, ethacrylic, α-chloroacrylic, crotonic, maleic, fumaric, itaconic acids, and the like.

In the ionomeric resins, metal ions, such as sodium, zinc, magnesium, lithium, potassium, calcium, etc., are used to neutralize some portion of the acid groups in the ionic copolymers, resulting in a thermoplastic elastomer exhibiting enhanced properties. While there are currently more than fifty commercial grades of ionomers available from DuPont and Exxon with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e. relative content of ethylene and methacrylic and/or acrylic acid groups), the degree of neutralization, etc., and wide number of additive ingredients which may be added to improve various characteristics of the stock compositions, including reinforcing materials such as glass fibers and inorganic fillers, softening agents such as plasticizers, and other compatible ingredients such as antistatic agents, antioxidants, stabilizers, processing acids, etc., a great deal of research continues in order to further enhance the physical/rheological properties of ionomeric resin polymer systems.

Summary of the Invention:

It has been surprisingly found that polycarboxylic acids can be used as additives to modify the physical properties of ionomeric resins. The present invention is thus directed to a novel polymeric composition containing a blend of an ionomeric polymer resin and from about 1 to about 20 pph, per 100 parts of ionomeric polymer resin, of a polycarboxylic acid.

The present invention also provides a process for modifying the rheological properties of ionomeric polymer resins involving blending the ionomers with from about 1 to about 20 pph, per 100 parts of ionomeric polymer resin, of a polycarboxylic acid.

Description of the Invention:

Other than in the operating examples or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions are understood as being modified in all instances by the term "about".

Any of a wide variety of ionomers may be used in the present invention. A preferred class of ionomers are copolymers of alpha-olefins containing, for example, about 2 to about 10, preferably 2 to 6 carbon atoms with from about 0.2 to 50 mol% and, preferably about 3 to 30 mol% of an unsaturated monocarboxylic acid having from about 3 to about 8 carbon atoms, in which up to 70% of the carboxyl groups are neutralized with cations having a valence of 1 to 3. Preferably, the neutralizing cations are metals from Groups IA, IIA, IIA, and th transitions elements of the Periodic Table, .g., transition elements such as zinc, alkalin earth metals such as calcium and magnesium, and alkali

metals such as sodium and potassium. The ionomer may have a molecular weight within a wide range as indicated, for example, by a number average molecular weight of from about 500 to about 500,000 or a melt index of from about 0.1 to about 1000 g/10 min as determined by ASTM-D-1238.

Suitable alpha-olefins which may be used in the preparation of the contemplated ionomers are ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, 3-methylbutene-1, and 4-methylbutene-1. The preferred alpha-olefin is ethylene.

The alpha, beta-ethylenically unsaturated carboxylic acids which can be copolymerized with the alpha-olefin preferably have 3 to 8 carbon atoms. Examples of such acids include acrylic acid, methacrylic acid, maleic acid, fumaric acid monoesters of dicarboxylic acids, such as methyl hydrogen maleate, methyl hydrogen fumarate, and ethyl hydrogen fumarate, and maleic anhydride, which is considered to be an acid in the present invention.

Although the olefin content of the ionic copolymer should be at least 50 mol percent, more than one olefin can be employed to provide the hydrocarbon segments of the copolymer. Moreover, more than one alpha, beta-ethylenically unsaturated carboxylic acid may also be employed. Additionally, any third copolymerizable monomer can be employed in combination with the olefin and the carboxylic acid comonomer. Preferred termonomers are vinyl esters and acrylates, e.g., vinyl alkanoates and alkyl acrylates and methacrylates having up to eight carbon atoms, such as vinyl acetate, vinyl propionate, methyl methacrylate, ethyl acrylate and isobutyl acrylate. Examples of suitable commercial ionomers are those sold by DuPont Company

under the trad mark SURLYN®.

A particularly preferred ionomer for use in the pr sent invention is the reaction product of ethylene and methacrylic acid. The reaction product thus formed preferably has a degree of neutralization of up to 100% of the ionomer, and most preferably from up to about 70%. The neutralization can be performed using ions selected from the group consisting of sodium, zinc, lithium, aluminum and potassium.

The polycarboxylic acids which may be employed in the present invention are, in general, those organic acids containing two or more carboxyl (COOH) groups. Dibasic acids ranging from succinic acid, i.e., 4 carbon diacids, to dimer acid, i.e., 36 carbon diacids, as well as 54 carbon trimer acids or those of higher functionality may also be used. A particularly preferred group of polycarboxylic acids are those selected from the group consisting of adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, dimer acid, and mixtures thereof, including their salts.

As mentioned above, it has been surprisingly found that polycarboxylic acids can be combined with ionomeric polymer resins in order to modify their rheological and physical properties. For example, by blending a multifunctional acid with an ionomer, one can modify the ionomer's tensile strength, flex modulus and peel strength.

According to one embodiment, a polymeric composition in accordance with th pr sent invention contains a blend of 100 parts by weight of an ionomer resin and from about 1 to about 20 parts by weight, and preferably

from about 2 to about 10 parts by w ight of a polycarboxylic acid per 100 parts of ionomer resin. The ionomer resin is preferably the reaction product of ethylene and methacrylic acid, with the resultant ionomer having a degree of neutralization of up to 100%, and most preferably up to about 70%. The polycarboxylic acid is preferably chosen from adipic acid, azelaic acid, sebacic acid, dodecanedioic acid and dimer acid, their salts, and mixtures thereof.

The novel polymeric composition of the invention formed by blending the ionomeric resin with the polycarboxylic acid, as stated above, can have a degree of neutralization of up to about 100% based on the novel polymeric composition as a whole, and preferably up to about 50%.

Auxiliaries may also be added to the polymeric composition such as, for example, dyes, optical brighteners, additional plasticizers and the like, in order to further alter the physical properties of the composition.

The polymeric composition of the present invention can be produced from either solution, from a melt phase or by dry blending. In this regard, the ionomeric resins and the polycarboxylic acids are blended in a Banbury type mixer, two-roll mill or extruded. In a particularly preferred embodiment of the invention, the polymeric composition is blended using a twin-screw extruder. The blended polymeric composition can then be formed into slabs or pellets and stored in such a state until molding.

It should be noted that while it is known in the art to modify the rheological/physical properties of ionomers by varying the polymer's chemical structure during its polymerization, the present invention utilizes compounding/bl nding techniques, which are significantly less costly than

changing the polymer's chemical structure, to achieve the same variation in physical properties.

The present invention will be better understood when read in light of the following examples, all of which are intended to be illustrative only and are not meant to limit the scope of the invention. Unless otherwise indicated, percentages are on a weight-by-weight basis.

Example 1

Polymeric compositions in accordance with the present invention were prepared by twin-screw extrusion and injection molded in order to evaluate their physical properties. The polymeric compositions were formed by blending 100 parts of SURLYN® 9910, which is a high acid (about 15% by weight) polymer, highly neutralized with zinc, with various polycarboxylic acids, in varying amounts. Their composition and physical properties are listed in Table 1 below.

Table 1

Example	Acid Type	PPH Acid	Peel Str. (#/inch)	Modulus (Kpsi)
1-1	NONE	0	3.7	47.3
1-2	Adipic	5.3	5.0	29.4
1-3	Azelaic	5.3	4.0	34.7
1-4	Sebacic	5.3	5.7	30.2
1-5	DDDA	5.3	4.7	33.8
1-6	Dimer	5.3	0.4	31.6
1-7	Dimer	9.5	0.3	25.0

Example 2

Polymeric compositions in accordance with the present invention were prepared by twin-screw extrusion and injection molded in order to evaluate their physical properties. The polymeric compositions were formed by blending 100 parts of NUCREL® 960, which is a high acid (about 15% by weight) polymer, with various polycarboxylic acids, in varying amounts. Their composition and physical properties are listed in Table 2 below.

Table 2

Example	Acid Type	PPH Acid	Peel Str. (#/inch)	Modulus (Kpsi)
2-1	NONE	0	3.7	13.9
2-2	Adipic	5.3	5.6	16.1
2-3	Azelaic	5.3	6.7	8.6
2-4	Sebacic	5.3	4.1	12.0
2-5	DDDA	5.3	3.1	12.6
2-6	Dimer	5.3	0.8	6.6

Example 3

Polymeric compositions in accordance with the present invention were prepared by twin-screw extrusion and injection molded in order to evaluate their physical properties. The polymeric composition were formed by blending 100 parts of NUCREL 960 or SURLYN® 9910 with disodium azelate. Their composition and physical properties are listed in Table 3 below.

Table 3

Example	Polymer	Acid Type	PPH Acid	Peel Str. (#/inch)	Modulus (Kpsi)
3-1	NUCREL® 960	NONE	0	3.7	13.9
3-2	NUCREL® 960	Disodium Azelate	5.3	4.0	21.4
3-3	SURLYN® 9910	NONE	0	3.7	47.3
3-4	SURLYN® 9910	Disodium Azelate	5.3	1.6	42.4

Example 4

Polymeric compositions in accordance with the present invention were prepared by twin-screw extrusion and injection molded in order to evaluate their physical properties. The polymeric composition were formed by blending 100 parts of SURLYN® 8920, which is a high acid (about 15% by weight) polymer, highly neutralized with sodium, with azelaic acid. Their composition and physical properties are listed in Table 4 below.

Table 4

Example	Acid Type	PPH Acid	Peel Str. (#/inch)	Modulus (Kpsi)
4-1	NONE	0	2.5	46.2
4-2	Azelaic	5.3	3.0	38.0

4-3	Disodium Azelate	5.3	2.2	49.5

Example 5

Polymeric compositions in accordance with the present invention were prepared on a Brabender Plasticorder and compression molded in order to evaluate their physical properties. The polymeric compositions were formed by blending 100 parts of NUCREL® 960 with azelaic acid, and then neutralized to 50% total neutralization level using NaOH. The blend compositions and physical properties are listed in Table 5 below.

Table 5

Example	Acid Type	PPH Acid	Peel Str. (#/inch)	Modulus (Kpsi)
5-1	NONE	0	Not Run	Not Run
5-2	Adipic	4.3	2.8	15.5
5-3	Azelaic	5.7	6.1	18.3
5-4	DDDA	6.8	3.0	25.0
5-5	Brassylic	7.0	2.3	14.7
5-6	Adipic	3.2	2.3	19.0
5-7	Azelaic	4.1	5.5	14.5
5-8	DDDA	5.0	2.3	18.9
5-9	Brassylic	5.4	2.9	15.5
5-10	Dimer	12.6	0.5	15.1
5-11	Dim r	5.5	1.2	18.0
5-12	Trimer	12.6	0.3	14.6

Example 6

Several blends were prepared by melt compounding 100 parts of SURLYN® 8920 or SURLYN® 9910 with various amounts of azelaic acid. Their composition and melt index are listed in Table 6 below.

Table 6

Example	Polymer	Acid Type	PPH Acid	MeltIndex @ 190 C (g/10min)
6-1	SURLYN® 8920	NONE	0	1.3
6-2	SURLYN® 8920	Disodium Azelate	5.3	1.6
6-3	SURLYN® 8920	Azelaic	0.5	1.6
6-4	SURLYN® 8920	Azelaic	2.1	2.3
6-5	SURLYN® 8920	Azelaic	5.3	6.1
6-6	SURLYN® 9910	NONE	0	1.9
6-7	SURLYN® 9910	Azelaic	5.3	7.2

Example 7

Polymeric compositions in accordance with the present invention were prepared on a Brabender Plasticorder and compression molded in order to evaluate their physical properties. The polymeric compositions were formed by blending 100 parts of NUCREL® 960 with azelaic acid, and then neutralized to 60-70% total neutralization level using Na, Mg, Zn and Al. The blend compositions and physical properties are listed in Table 7 below.

Table 7

Example	PPH Azelaic	Cation	% Neutr.	Peel Str. (#/inch)	Modulus (Kpsi)
7-1	16.5	Na	70	1.5	12.3
7-2	16.5	Na	60	5.0	
7-3	4.1	Na	60	1.8	15.9
7-4	16.5	Mg	70	4.5	6.0
7-5	16.5	Zn	70	6.6	8.3
7-6	16.5	Al	70	0.5	10.7

What is claimed is:

1. A polymer composition comprising:

(a) 100 parts by weight of an acid-containing polymer or ionomeric resin; and

(b) from about 1 to about 20 parts by weight of a polycarboxylic acid or a salt thereof, based on the weight of component (a).

2. The composition of claim 1 wherein the ionomeric resin has a degree of neutralization up to about 100%.

3. The composition of claim 1 wherein component (a) is a reaction product of an olefin having from about 2 to about 10 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to about 8 carbon atoms.

4. The composition of claim 1 wherein the polycarboxylic acid is selected from the group consisting of adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, dimer acid, their salts, and mixtures thereof.

5. The composition of claim 1 wherein component (a) has a degree of neutralization up to about 70%.

6. The composition of claim 5 wherein component (a) is neutralized with ions selected from the group consisting of sodium, zinc, lithium, aluminum and potassium.

7. The composition of claim 1 wherein component (b) is present in the polymer composition in an amount of from about 2 to about 10 parts by weight based on the weight of component (a).

8. Th composition of claim 3 wherein the olefin is ethylene.

9. The comp sition of claim 3 wher in the unsaturated monocarboxylic

acid is m thacrylic acid.

10. A polymeric composition comprising:

(a) 100 parts by weight of an ionomeric resin based on a neutralized reaction product of ethylene and methacrylic acid; and

(b) from about 1 to about 20 parts by weight of a polycarboxylic acid selected from the group consisting of adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, dimer acid and their salts, wherein the polymeric composition has a degree of neutralization of up to about 50%.

11. A process for modifying the physical properties of a polymer composition comprising the steps of:

(a) providing 100 parts by weight of an acid-containing polymer or ionomeric resin;

(b) providing from about 1 to about 20 parts by weight of a polycarboxylic acid or a salt thereof, based on the weight of component (a);

(c) blending components (a) and (b) to form a polymer composition; and

(d) neutralizing up to about 100% of the polymer composition.

12. The process of claim 11 wherein the acid-containing polymer or ionomeric resin has a degree of neutralization of up to about 70%.

13. The process of claim 11 wherein the ionomeric resin is a neutralized reaction product of an olefin having from about 2 to about 10 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to about 8 carbon atoms.

14. The process of claim 11 wherein th polycarboxylic acid is selected from the group consisting of adipic acid, azelaic acid, sebacic acid, dodecanedioic

acid, and their salts.

15. The process of claim 11 wherein the polymer composition has a degree of neutralization of up to about 50%.

16. The process of claim 11 wherein the polymer composition is neutralized with ions selected from the group consisting of sodium, zinc, lithium, aluminum and potassium.

17. The process of claim 11 wherein component (b) is present in an amount of from about 2 to about 10 parts by weight, based on the weight of component (a).

18. The process of claim 13 wherein the olefin is ethylene.

19. The process of claim 13 wherein the unsaturated monocarboxylic acid is methacrylic acid.

20. A process for modifying the physical properties of a polymer composition comprising the steps of:

(a) providing 100 parts by weight of an ionomeric resin based on a neutralized reaction product of ethylene and methacrylic acid;

(b) providing from about 1 to about 20 parts by weight of a polycarboxylic acid selected from the group consisting of adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, their salts, and mixtures thereof, based on the weight of component (a);

(c) blending components (a) and (b) to form a polymer composition; and

(d) neutralizing up to about 50% of the polymer composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/11724

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 20/02, 8/14
US CL :524/321; 525/327, 386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/321; 525/327, 386

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,296,522 A (VOGT et al.) 22 March 1994, columns 2-6.	1-20
X	US 4,611,017 A (MCKINNEY et al.) 09 September 1986, columns 2-6.	1-20
X	US 4,602,058 A (GRAHAM et al.) 22 July 1986, columns 5-7 and abstract.	1-20
X	US 4,500,664 A (MCKINNEY et al.) 19 February 1985, columns 2-4.	1-20
X	US 4,136,069 A (VACHON et al.) 23 January 1979, columns 1-4.	1-20
X	US 3,620,878 A (GUTHRIE) 16 November 1971, columns 2-4 and abstract.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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